



# Progress Report

NASA Grant NsG-192-61/09-015-001

## UNPUBLISHED PRELIMINARY DATA

During the six month period extending from February 1, 1964 through July 31, 1964 work performed in this laboratory covered two particular areas of endeavor. These included:

A) Additional basic studies involving certain ionization phenomena in gases in an effort to better understand those processes responsible for the highly sensitive responses to the presence of permanent as well as other gaseous samples in ionization detectors used for gas chromatography.

B) The development of a broad based long term basic research program investigating certain parameters involved in the use of a combined gas chromatography-mass spectrometry techniques for the analysis of various gases comprising planetary atmospheres as well as the analysis of planetary surfaces for the presence of organic compounds.

With reference to Part A:

The technique of competitive quenching has been used to determine the relative rate constants of  $O_2, N_2, H_2, CO_2$ , and  $CH_4$  for quenching of excited argon atoms formed both by the action of  $\beta$  radiation from a tritium source and also by low-energy electron impact. Calculations based on the mean lifetime of these species in the system show that with the exception of nitrogen the quenching process for all the other molecules is highly efficient and energy transfer occurs on every collision. Evidence is also presented to suggest that the excited species formed by collision with  $\beta$  rays are primarily in the  $^1P_1$  state and not the  $^3P_{0,2}$  metastable states.

This has resulted in a publication entitled:

Energy Transfer between Molecules and Electronically Excited Atoms. Journal of Chemical Physics, 41, 2021, 1961 by M.M. Shahin and S.R. Lipsky.

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With reference to Part B:

Most recently, a technological development has been reported by Ryhage of the Karolinska Institute, Stockholm, Sweden (Analytical Chemistry 36, 759, 1964) which appears to be of key importance in the development of an 'ideal' system for the detection and precise identification of organic compounds on planetary surfaces. Moreover, it now seems plausible to assume that if necessary such a system could be designed to also provide a complete analysis of the atmospheres of a planet during descent as well as upon settling on its surface.

In essence, Ryhage has described a very elegant dynamic method whereby a sample component vapor eluted from a gas chromatographic column by means of a carrier gas can be concentrated many fold via a pair of molecular separators and fed directly into the ion source of a mass spectrometer for identification purposes. Apparently the 'separators' adapted from the work of E.W. Becker provide very rapid effusion of the relatively large quantities of the lighter carrier gas (helium or hydrogen) thus giving rise to a high enrichment coefficient, short time constant, and small effective dead volume all of which lead to optimal conditions for mass spectrometer operation. Under these circumstances in conjunction with a high speed scanning and recording system it was possible to procure mass spectra every 1 to 2 seconds (mass range  $m/e$  12 to 500) of the component bands as they emerged from the gas chromatographic column.

Prior to this time the use of combined gas chromatography - mass spectrometry techniques for the characterization of individual component bands as they continuously emerged from the gas chromatographic column has been wrought with difficulties. Satisfactory results usually have been confined to the analyses of highly volatile low molecular weight hydrocarbons. In studies involving the more complex and less volatile higher molecular weight moieties of biochemical importance samples eluted from the column by necessity were usually trapped out and then introduced into the mass spectrometer. As noted by others in the field for this application this adynamic system was exceedingly time consuming and had many disadvantages associated with the collection, handling, and introduction of the sample.

It became apparent that with the very recent availability of molecular separators to optimally enrich and continuously feed the effluent from the gas chromatographic column into a high resolution, rapid scan mass spectrometer (mass range  $m/e$  12 to 500 every 1-2 seconds) these difficulties are a thing of the past and the analytical horizons have been greatly extended. It became obvious that with the exceedingly high quality of mass spectral data available under these conditions one is now in position to conveniently and reliably determine the structures of complex molecules separated by the highly efficient gas chromatographic technique.

In the light of this fascinating development a line of investigation is being pursued in collaboration with JPL in an effort to provide information which should lead to the design and production of one of the most effective and versatile systems for extraterrestrial life detection to date.

Many scientists acquainted with the problems inherent in the detection and identification of organic compounds on planetary surfaces agree that one of the most feasible approaches here involves the use of controlled 'pyrolysis' of surface samples with subsequent separation of volatile, semi-volatile and then degradation products by means of high resolution gas chromatographic columns. With the advent of the aforementioned advances in mass spectrometry a complete mass spectra of each individual degradation product that can be separated in this manner can be made available for positive structural identification in a matter of seconds. With this information at hand it should be possible to predict with a high degree of certainty the chemical nature of the original organic moieties present in the sample prior to degradation. Thus in sharp contrast to certain 'growth' or 'wet' chemistry systems for life detection where one may obtain an equivocal yes or no answer, this experiment should provide a wealth of information in the form of reliable, precise and familiar data that will serve as the corner stone for subsequent and more sophisticated Missions. The achievement of this goal can now be greatly facilitated by the building up of a hard core of basic knowledge in several collaborating laboratories. Accordingly, with the collaboration of JPL we are now in the process of "tooling up" in an effort to employ a gas chromatography-mass spectrometry techniques forthwith in order to study optimal conditions for:

a) the 'pyrolysis'\* of a range of materials extending from pure compounds of biochemical importance to soil and rock samples from significantly different environments.

This will involve:

1. Effects of sample size, influence of sample constituents, temperature, carrier gas flow rate, and duration of pyrolysis procedure upon the formation of pyrolysis products.

b) the separation and identification of the by products of pyrolysis by these procedures.

This will involve:

1. The use of high efficiency gas solid and gas liquid chromatography columns of different types i.e. packed conventional columns, open capillary, and packed capillary columns. A wide range of polar and non-polar stationary phases will be utilized

in the study in an effort to separate the greatest number of components in order to facilitate eventual identification by means of comparative retention times and mass spectrometry.

\* In practice only the final temperature cycle will strictly involve the process of pyrolysis and the analysis of degradation products. Prior temperature cycles ( $\approx 40-125^{\circ}\text{C}$ ,  $125^{\circ}-250^{\circ}\text{C}$ , etc) will be utilized to release intact volatile and semi-volatile components with subsequent separation and identification by gas chromatography-mass spectrometry.